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The ytterbium–copper–aluminium system

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Abstract

The isothermal section of the Yb–Cu–Al phase diagram at 870 K over the whole concentration region has been constructed using X-ray structure and phase analysis. We have confirmed the existence of earlier reported ternary compounds: YbCuAl (ZrNiAl type) and $YbCu_4Al_8$ ($CeMn_4Al_8$ type); the previously reported compound $YbCu_4Al$ proved to be a solid solution of aluminium in the binary compound $YbCu_5$ ($CaCu_5$). New ternary aluminides such as $Yb_4(Cu_{0.26}Al_{0.74})_{33}$ (new structure type), $Yb_2(Cu_{0.57}Al_{0.43})_{17}$ (Th_2Zn_{17}), $Yb(Cu_{0.85}Al_{0.15})_6$ ($YbMo_2Al_4$), $Yb_6(Cu_{0.74}Al_{0.26})_{23}$ (Th_6Mh_{23}) and $Yb(Cu_{0.30}Al_{0.70})_3$ ($PuNi_3$) have been prepared for the first time and their crystal structures have been determined. The limits of solid solutions of the binary compound $YbCu_5$ and the homogeneity ranges of the ternary phases $Yb(CuAl)_{12}$, $Yb(CuAl)_{17}$ and $Yb(CuAl)_2$ have been established.

1. Introduction

The Yb–Cu–Al system was studied in part only to obtain a number of compounds having definite compositions and structures [1]. The existence was reported of such ternary compounds as: $YbCu_4Al$ ($CaCu_5$-type structure $a=0.5044$ nm, $c=0.4140$ nm) [2], $YbCuAl_3$ ($BaAl_4$-type, $a=0.4293$ nm, $c=1.0654$ nm) [3] and YbCuAl(ZrNiAl-type $a=0.6926$ nm, $c=0.3986$ nm) [4]. Constant compositions were assigned for all these compounds. Taking into account that ternary compounds in the Ln–Cu–Al systems (where Ln is a rare earth metal) are usually characterized by variable compositions, the homogeneity ranges of these compounds have to be redetermined. Therefore, our study was carried out with the purpose of investigating the isothermal section of the Yb–Cu–Al equilibrium phase diagram in the whole concentration region and determining the crystal structure of the existing compounds together with the limit of their homogeneity ranges.

Binary compounds in the systems Yb–Cu, Cu–Al and Yb–Al have been studied widely. According to Palenzona [5] $YbAl_2$ is formed from the liquid state at 1673 K and $YbAl_3$ by peritectic reaction at 1253 K. The most extensive investigation of the Yb–Cu system was performed by Iandelli and Palenzona [6] and revealed the existence of the following compounds: $YbCu_5$, Yb_2Cu_9, Yb_2Cu_7, $YbCu_2$ and YbCu. The Yb_2Cu_9 phase melts congruently at 1210 K, while the others were formed by peritectic reactions at 1152, 1098, 1030 and 901 K, respectively. Hornstra and Buschow [7] reported on $YbCu_{6.5}$ ($a=0.5004$, $c=0.4118$ nm) composition for the compound with $CaCu_5$-type structure. The compound Yb_6Cu_{23} with Th_6Mn_{23} structure ($a=1.203$ nm) was obtained by Tsvashenko [8] at high pressure. We used data on the Cu–Al system given in ref. 9.

2. Experimental details

The samples for investigation were prepared by direct arc melting of pure components with certified purity of 99.9 wt.% for Yb and 99.99 wt.% for Cu and Al. Powders of the constituent elements were pressed into pellets and then arc melted under an argon atmosphere at normal pressure. The copper powder was reduced using dried hydrogen at 570 K [10]. All of the alloys prepared were heat treated at 870 K in quartz ampoules which were filled with pure argon. The samples containing 0–45 at.% Cu and 0–33 at.% Yb were heated for 600 h and all others for 1500 h. The alloys were quenched in cold water without breaking the ampoules.

Phase analysis was carried out using X-ray powder film data obtained by the Debye–Scherrer technique using Cr K radiation. Lattice constants were determined from the powder patterns (diffractometer DRON-3M, Cu Kα radiation); all calculations were performed using CSD software created by Akselrud et al. [11].

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3. Results

During our investigations of equilibrium diagrams of the ternary system Yb–Cu–Al we confirmed the existence of several known binary and ternary compounds: $YbAl_2$, $YbAl_3$, $YbCu_5$, $YbCu_2$, YbCu, YbCuAl and $YbCu_4Al_8$. The compounds Yb_6Cu_{23}, $YbCu_{6.5}$, Yb_2Cu_9 and Yb_2Cu_7 were not observed by us at 870 K. We found that the previously reported phase $YbCu_4Al$ is actually a solid solution of aluminum in the binary compound $YbCu_5$. The limiting composition of this solid solution is given by the formula $YbCu_{2.9}Al_{2.1}$. The compound $YbAl_2$ can dissolve up to 17 at.% copper. The variation in lattice constants and unit cell volumes of the above-mentioned solid solutions are shown in Fig. 1(a) and (b). All other binary compounds dissolve less than 5 at.% of the third component, which does not lead to appreciable changes in the lattice parameters.

The ternary compounds $Yb_4(Cu_{0.26}Al_{0.74})_{33}$ (new structure type), $Yb_2(Cu_{0.57}Al_{0.43})_{17}$ (Th_2Zn_{17} type), $Yb(Cu_{0.85}Al_{0.15})_6$ ($YbMo_2Al_4$ type), $Yb_6(Cu_{0.74}Al_{0.26})_{23}$ (Th_6Mn_{23}type) and $Yb(Cu_{0.70}Al_{0.30})_3$ were synthesized for the first time. Crystallographic data are listed in Table 1 (the results of investigating the crystal structures of these compounds are reported in a separate publication. The Yb–Cu–Al equilibrium diagram at 870 K is shown in Fig. 2.

Compounds with $ThMn_{12}$ and Th_2Zn_{17} structures have homogeneity ranges. Replacement of copper atoms ($r=0.127$ nm) by aluminium atoms ($r=0.144$ nm) resulted in increased lattice constants and unit cell volumes for these compounds (Fig. 1(c) and (d)).

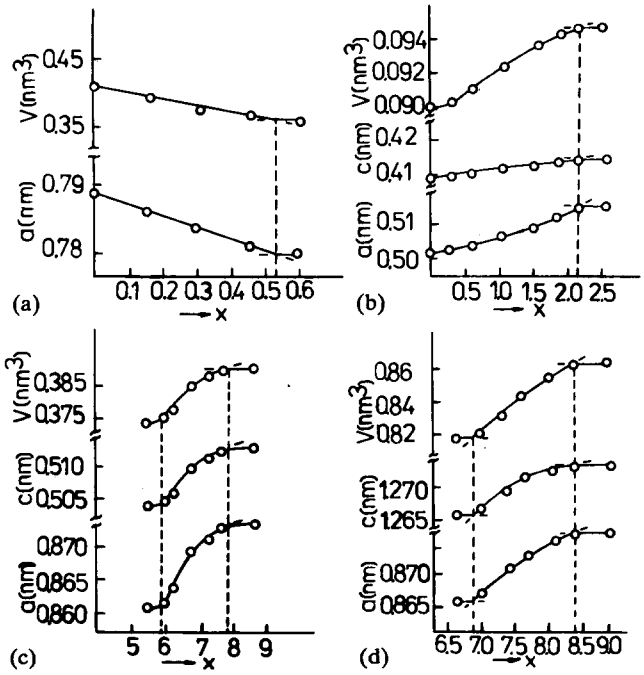

Fig. 1. Lattice parameters and cell volumes of solid constructions (a) $YbAl_{2-x}Cu_x$, (b) $YbCu_{5-x}Al_x$, (c) $YbCu_{12-x}Al_x$ and (d) $Yb_2Cu_{17-x}Al_x$.

4. Discussion

Up to now the ternary systems Ln–Cu–Al, where Ln is a rare earth metal have been studied relatively comprehensively: phase diagrams for the ternary systems Y–Cu–Al (part of the system), Gd–Cu–Al, Dy–Cu–Al, Ho–Cu–Al, Er–Cu–Al and Lu–Cu–Al have been proposed by Zarechnyuk and Kolobnjev [13], Prevarsky and Kuz'ma [14], Kuz'ma and Miljan [15], Stel'makhovych [16], Kuz'ma and Pan'kiv [17] and Stel'makhovych *et al.* [18], respectively. The existence of compounds such as $Ln_2(CuAl)_{17}$, $Yb_4(Cu_{0.26}Al_{0.74})_{33}$, $LnCu_{2-x}Al_{2+x}$, $Ln_6(CuAl)_{23}$ and LnCuAl was revealed, and their crystal structure were determined by Prevarsky and Kuz'ma [19], Dwight *et al.* [20] and Stel'makhovych and Kuz'ma [3, 12, 21], respectively. Therefore, our investigation of the ternary system Yb–Cu–Al and results obtained on the crystal structure of compounds $Ln(CuAl)_3$ and $Yb(Cu_{0.85}Al_{0.15})_6$ permit us to reach some conclusions.

Most of the structures formed in the ternary systems Ln–Cu–Al (except for ZrNiAl-type structures) belong to a category with icosahedral coordination of the smallest atoms (Cu and Al). These ternary compounds are characterized by statistical distribution of copper and aluminium atoms, and as a result they have considerable homogeneity ranges with constant rare earth metal contents.

At present, the ternary systems Tb–Cu–Al and Tm–Cu–Al have been studied less thoroughly. However, by taking into consideration the data on the crystal structures of ternary aluminides listed in Fig. 3, we can predict the existence of compounds with a $ThMn_{12}$-type structure.

The considerations for $Ln(CuAl)_5$ compound formation have to be discussed separately. In binary Ln–Cu systems morphotropic transitions from $CaCu_5$ to $AuBe_5$ structure types are observed. Binary compounds $LnCu_5$ with Ln≡Y, Yb belong to the $CaCu_5$-type structure, and those with Ln≡Dy, Ho, Er, Tm, Lu belong to the $AuBe_5$ type. Compounds $GdCu_5$ and $TbCu_5$ can form in both types, with temperature-dependent polymorphous transformation. This has an influence on the ternary systems Ln–Cu–Al. The existence of compounds with $CaCu_5$-type structure in binary Ln–Cu systems leads to the formation of a considerable number of solid solutions in the corresponding ternary system with aluminium (Ln≡Y, Gd, Tb). If a compound with $CaCu_5$-type structure does not exist in the binary system, a ternary compound $Ln(CuAl)_5$ is formed. This is the case in the Ln–Cu–Al systems with Ln≡Dy, Ho, Er,

TABLE 1. Crystallographic data for ternary compounds of the Yb–Cu–Al system

Compound	Structure type	Space group	Lattice parameter (nm)		Reference
			a	*c*	
$Yb(Cu_{0.50-0.33}Al_{0.50-0.67})_{12}$	$ThMn_{12}$	*I4/mmm*	0.8623–0.8724	0.5057–0.5118	[a]
$Yb_2(Cu_{0.51-0.46}Al_{0.49-0.54})_{17}$	Th_2Zn_{17}	*R3̄m*	0.8653–0.8877	1.2659–1.2734	[a]
$Yb_4(Cu_{0.26}Al_{0.74})_{33}$	New type	*I4/mmm*	0.8565	1.6255	21
$Yb(Cu_{0.85}Al_{0.15})_6$	$YbMo_2Al_4$	*I4/mmm*	0.63866	0.4926	[a]
$Yb_6(Cu_{0.74}Al_{0.26})_{23}$	Th_6Mn_{23}	*Fm3m*	1.2234	–	12
$Yb(Cu_{0.30}Al_{0.70})_3$	$PuNi_3$	*R3̄m*	0.5471	2.5358	[a]
$Yb(Cu_{0.55-0.50}Al_{0.45-0.50})_2$	ZrNiAl	*P62m*	0.6913–0.6925	0.3983–0.3990	[a]

[a]Data from this work

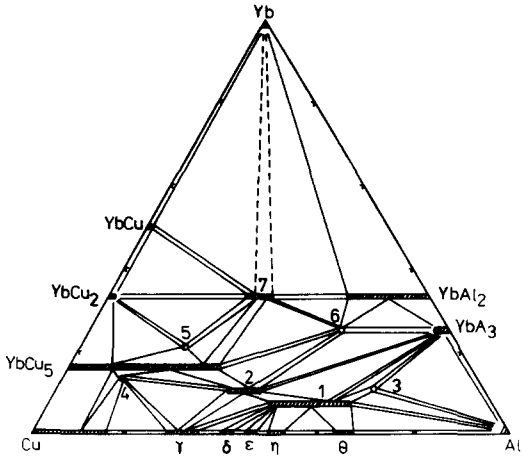

Fig. 2. Isothermal section of the Yb–Cu–Al phase diagram at 870 K.

Struct.type	Y	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$ThMn_{12}$									
Th_2Zn_{17}									
$Yb_4(Cu,Al)_{33}$									
$YbMo_2Al_4$									
$CaCu_5$									
$BaAl_4$									
$CeNi_{2-x}Sb_{2+x}$									
Th_6Mn_{23}									
$PuNi_3$									
ZrNiAl									

Fig. 3. Structure types of known ternary aluminides in the systems Ln–Cu–Al.

Lu. Consequently, in the system Tm–Cu–Al, formation of a ternary compound $Tm(CuAl)_5$ with $CaCu_5$-type structure is quite possible.

All the compounds $LnNi_5$, where Ln is a heavy rare earth metal, display $CaCu_5$-type structure, but for $LnCu_5$, as was already noted above, the $CaCu_5$ and $AuBe_5$ types are observed. Consequently, replacement of Ni atoms by Cu atoms leads to an increasing number of valence electrons (s and d) and to decreasing stability of the $CaCu_5$-type compounds. Replacement of copper by aluminium leads to a decrease in the overall number of electrons in the unit cell and favours conditions for $CaCu_5$-type formation. This might be a reason why ternary compounds with $CaCu_5$-type structure are formed in ternary Ln–Cu–Al systems.

Figure 4 illustrates the dependence of the unit cell volumes of isostructural compounds on the atomic number of the rare earth component. It can be inferred from these data that Yb atoms are in a normal valence state equal to Yb^{3+}. Only in the compound with $PuNi_3$-type structure has ytterbium the Yb^{2+} or intermediate valence state, as may be derived from the pronounced maximum in Fig. 4. The compounds $Yb_4(Cu_{0.26}Al_{0.74})_{33}$ and $Yb(Cu_{0.85}Al_{0.15})_6$ have no isostructural compounds in related Ln–Cu–Al systems, and because of this other methods must be used for finding the valence state of the ytterbium atoms.

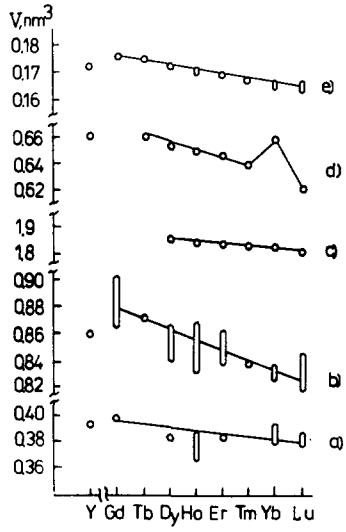

Fig. 4. Cell volumes of isostructural compounds in the systems Ln–Cu–Al.

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